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Overcoming the shortcomings of the Nernst–Planck model

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This is a study on electrolytes that takes a thermodynamically consistent coupling between mechanics and diffusion into account. It removes some inherent deficiencies of the popular Nernst–Planck model. A boundary problem for equilibrium processes is used to illustrate the features of the new model.

1 Introduction

The development of the thermodynamic theory of irreversible processes with coupling of mechanics, diffusion, heat conduction, chemical reactions and electromagnetic fields started in 1940 and its classical version is more or less completed in 1959 when J. Meixner and H. G. Reik published the article *Thermodynamik der irreversiblen Prozesse* in the Encyclopedia of Physics.[1] In this study we propose a model for electrolytes that completely relies on classical thermodynamics of irreversible processes.

The essential novelty of the proposed electrolyte model results from a thermodynamically correct coupling of diffusion and mechanics. In fact, it is remarkable that in the available electrolyte models this coupling is either not included or it is introduced in a thermodynamically incorrect way, see the survey of the literature below. Our model removes difficulties of the old Nernst–Planck model proposed in 1890, which is today very popular and still used by many authors. For a mixture of N constituents the Nernst–Planck model proposes N diffusion equations and does not take care of the fact that the sum of these equations over all constituents must give the conservation law of mass for the total mixture. A further shortcoming of the Nernst–Planck model is the missing coupling to the balance equation for the momentum, which serves to determine the evolution of the solvent.

The paper is organized as follows:

In Section 2 we present our main results. Section 2.1 gives a short introduction to the model. In Section 2.2 we use this model to calculate equilibrium processes with a prescribed voltage between two electrodes. A survey of the available literature and in particular a comparison of the new model with existing models is carried out in Section 2.3.

Sections 3–7 contain the details of our study. In Section 3 we present a careful discussion of the electrolyte model. Section 4 formulates a simple boundary problem that serves to illustrate various properties of the model. In Section 5 we introduce the notion of incompressibility and carry out the incompressible limit of our equations. Preliminary analytic calculations, which are necessary before a numerical treatment becomes possible, are found in Sections 6 and 7. In particular Section 7 is important because the model generates thin boundary layers that we treat by the methods of asymptotic analysis.

Finally, in Section 8 we describe in detail the numerical method for the complete solution to the boundary problem presented in Section 4.

2 Results and discussion

In this section we give a presentation and first discussions of our main results. Here we avoid subtleties of the derivation and various definitions of the involved quantities. Thus the section assumes some preexisting knowledge of the reader. The detailed derivation of the results is found in the subsequent sections.

2.1 Electrolyte model

We study a ternary electrolyte consisting of cations (C), anions (A) and a neutral solvent (S). We assume isothermal conditions and do not permit chemical reactions. The force of gravity is ignored. In the mixture we have two electrodes that are connected to a high resistance voltage source so that equilibrium is established.

The objective is the determination of the four variables

- number densities of the constituents n_C, n_A and n_S,
- electric potential φ as functions of space.

In Section 3 we derive a quite general model describing the evolution of the electrolyte which relies on the balance

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equations of mass, balance equations of momentum and the Poisson equation. In the stationary case, the general model (54)–(60) can be reduced to

$$\operatorname{div}(\boldsymbol{J}_\alpha) = 0 \quad \text{for } \alpha \in \{\mathrm{A},\mathrm{C}\}, \tag{1}$$

$$\nabla p = -n^{\mathrm{F}}\nabla\varphi, \tag{2}$$

$$-\varepsilon_0(1+\chi)\Delta\varphi = n^{\mathrm{F}}, \tag{3}$$

where p denotes the elastic pressure, $n^{\mathrm{F}} = z_{\mathrm{C}}e_0 n_{\mathrm{C}} + z_{\mathrm{A}}e_0 n_{\mathrm{A}}$ is the number density of free charges and the constants are: the dielectric constant ε_0, elementary charge e_0, the charge numbers of cations and anions z_{A}, z_{C} and the dielectric susceptibility χ.

The diffusion fluxes $\boldsymbol{J}_\alpha$ are of the form

$$\boldsymbol{J}_\alpha = -\sum_{\beta\in\{\mathrm{A},\mathrm{C}\}} M_{\alpha\beta}\left(\nabla\frac{\mu_\beta-\mu_{\mathrm{S}}}{T} + \frac{1}{T}\frac{z_\beta e_0}{m_\beta}\nabla\varphi\right) \quad \text{for } \alpha\in\{\mathrm{A},\mathrm{C}\}, \tag{4}$$

where μ_{C}, μ_{A} and μ_{S} are the chemical potentials of the constituents. The kinetic matrix $M_{\alpha\beta}$ is positive definite. The temperature is denoted by T.

We consider an ideal elastic mixture which is characterized by the following constitutive laws

$$p = p^{\mathrm{R}} + K\left(\frac{n}{n^{\mathrm{R}}} - 1\right), \tag{5}$$

$$g_\alpha = g_\alpha^{\mathrm{R}} + \frac{K}{m_\alpha n^{\mathrm{R}}}\ln\left(1 + \frac{p-p^{\mathrm{R}}}{K}\right). \tag{6}$$

$$\mu_\alpha = g_\alpha + \frac{kT}{m_\alpha}\ln(y_\alpha) \tag{7}$$

The index R indicates the reference state. The new constants are: atomic masses m_α, Boltzmann constant k, bulk modulus K of the mixture and specific Gibbs energies g_α of the pure constituents. These representations suggest to change the variables from $(n_{\mathrm{C}}, n_{\mathrm{A}}, n_{\mathrm{S}}, \varphi)$ to $(y_{\mathrm{C}}, y_{\mathrm{A}}, n, \varphi)$ with

$$n = \sum_{\alpha\in\{\mathrm{C},\mathrm{A},\mathrm{S}\}} n_\alpha \quad \text{and} \quad y_\alpha = \frac{n_\alpha}{n} \quad \text{for } \alpha\in\{\mathrm{A},\mathrm{C},\mathrm{S}\}. \tag{8}$$

The quantities y_α are the atomic fractions and n is the total number density of particles in the mixture.

The new model relies on the crucial observation that the N partial densities n_α are determined by only $N-1$ diffusion equations and the momentum balance. Let us discuss this in more detail: obviously we have N partial mass balances for the densities $\rho_\alpha := m_\alpha n_\alpha$ with corresponding mass fluxes $\rho_\alpha \boldsymbol{v}_\alpha = \rho_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha$,

$$\frac{\partial\rho_\alpha}{\partial t} + \operatorname{div}(\rho_\alpha\boldsymbol{v} + \boldsymbol{J}_\alpha) = 0. \tag{9}$$

Here, $\boldsymbol{v}$ is the barycentric velocity implying the side condition $\sum_{\alpha=1}^{N}\boldsymbol{J}_\alpha = 0$, *cf.* (24)–(26) below. Thus we can split off the partial mass balances into $N-1$ diffusion equations and the balance for the mass density $\rho = \sum_{\alpha=1}^{N} m_\alpha n_\alpha$ of the mixture,

$$\frac{\partial\rho}{\partial t} + \operatorname{div}(\rho\boldsymbol{v}) = 0. \tag{10}$$

In the general case where the barycentric velocity $\boldsymbol{v}$ is not zero, the variables ρ and $\boldsymbol{v}$ are determined by the combined system of balance equations for total mass and momentum. However, for equilibria with vanishing barycentric velocity $\boldsymbol{v} = 0$, the total mass balance (eqn (10)) cannot be used to determine ρ. Rather, the mass density ρ is determined by the static momentum balance (eqn (2)).

We can proceed in two alternative ways:

(1) We take care for the elasticity of the liquid mixture, *i.e.* we have an elastic constitutive law relating the material pressure to the total number density n. Then the static momentum equation determines n. However, due to the appearance of the Lorentz force, the momentum balance is coupled to the other equations.

(2) In the context of liquid mixtures, it is often a good approximation to consider an incompressible mixture. Then the momentum balance becomes an equation that determines the pressure field in the mixture. Because the treatment of this case is simpler than the first alternative, we choose the incompressible limit.

2.2 Results for 1D equilibrium states of incompressible mixtures

We consider the 1D version of the coupled system (1)–(7) on the domain $[0, L]$ and study its stationary solution subject to the boundary data

$$\varphi|_{x=0} = \varphi_L, \quad \varphi|_{x=L} = \varphi_{\mathrm{R}} \tag{11}$$

$$J_\alpha|_{x=0} = J_\alpha|_{x=L} = 0 \quad \alpha\in\{\mathrm{A},\mathrm{C}\}. \tag{12}$$

In particular, we are interested in an incompressible mixture that is described by the limit $K\to\infty$. Our main results are:

(1) The diffusion equations and the momentum balance can be solved to obtain the three atomic fractions in terms of the electric potential. For $\alpha\in\{\mathrm{A},\mathrm{C},\mathrm{S}\}$ we have

$$y_\alpha = c_\alpha\exp\left(-\frac{z_\alpha e_0}{kT}\varphi - \frac{1}{2}\frac{\varepsilon_0(1+\chi)}{kTn^{\mathrm{R}}}(\nabla\varphi)^2\right), \tag{13}$$

where the c_α are positive constants of integration. The coupling between diffusion and mechanics is reflected in eqn (13) by the contribution of $\nabla\varphi$ to the atomic fractions. It does not appear in any other electrolyte model. In this study we will demonstrate that the $\nabla\varphi$ contribution is of most importance. If the gradient terms were absent formula (13) is usually called the Boltzmann law and after inserting the Boltzmann law in the Poisson equation, the resulting equation is called the Poisson–Boltzmann equation.

(2) By no means it is evident that eqn (13) also holds for the neutral solvent with $z_{\mathrm{S}} = 0$. While the representations of y_{C} and y_{A} follow from the integration of the two diffusion equations, the atomic fraction y_{S} of the solvent follows from a combination of the diffusion equations and the momentum balance. Note that the representation (13) and the side condition $y_{\mathrm{C}} + y_{\mathrm{A}} + y_{\mathrm{S}} = 1$ imply

$$0 < y_\alpha(x) < 1 \quad \text{for} \quad x\in[0,L] \text{ and } \alpha\in\{\mathrm{A},\mathrm{C},\mathrm{S}\}. \tag{14}$$

(3) In order to calculate the atomic fractions from eqn (13), we have to solve the Poisson equation for the electric potential.

The Poisson equation induces the characteristic length scale of the system,

$$\sqrt{\frac{\varepsilon_0(1+\chi)kT}{e_0^2 n^{\mathrm{R}}}} \approx 10^{-10}\ \mathrm{m}, \tag{15}$$

that gives rise to sharp boundary layers at the electrodes with large variations of φ. To resolve these boundary layers with numerical methods, we apply formal asymptotic analysis to the Poisson equation. To this end we decompose the domain into the bulk region and the boundary layer at the left and right. Then we rescale these three regions in different ways and formulate matching conditions, see Fig. 1.

(4) Fig. 1 and 2 suggest that away from the electrodes, *i.e.* in the bulk region, the atomic fractions and the electric potentials are constant with values Y_{C}, Y_{A}, Y_{S} and Φ. These values are calculated from:

$$Y_\alpha = \bar{y}_\alpha \ \text{ for } \ \alpha = \mathrm{A,C}, \tag{16}$$

$$Y_{\mathrm{S}} = 1 - Y_{\mathrm{A}} - Y_{\mathrm{C}}, \tag{17}$$

$$\Phi = \varphi_{\mathrm{R}} + \frac{kT}{(z_{\mathrm{A}} - z_{\mathrm{C}})e_0} \ln\left(\frac{z_{\mathrm{A}}}{z_{\mathrm{C}}} \frac{1 - \exp\left(\frac{z_{\mathrm{C}} e_0}{kT}(\varphi_{\mathrm{R}} - \varphi_{\mathrm{L}})\right)}{1 - \exp\left(\frac{z_{\mathrm{A}} e_0}{kT}(\varphi_{\mathrm{R}} - \varphi_{\mathrm{L}})\right)} \right), \tag{18}$$

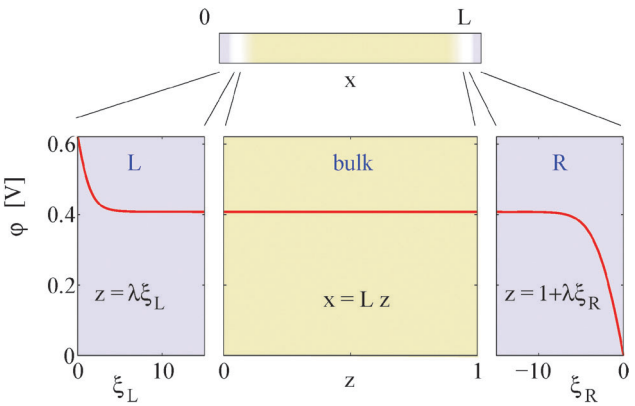

Fig. 1 Top: domain decomposition and numerically computed potential φ in the rescaled subdomains for boundary values $\varphi_{\mathrm{L}} - \varphi_{\mathrm{R}} = 0.62$ V, mean atomic fractions $\bar{y}_{\mathrm{A}} = 0.12$ and $\bar{y}_{\mathrm{C}} = 0.24$ and charge numbers $z_{\mathrm{A}} = -2$ and $z_{\mathrm{C}} = 1$.

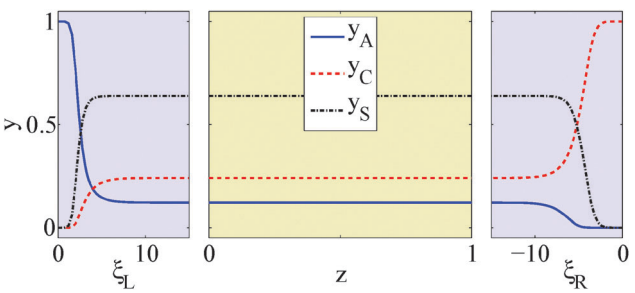

Fig. 2 Atomic fractions y_{A}, y_{C} and y_{S} in the boundary regions and in the bulk for the situation of Fig. 1.

where $\bar{y}_\alpha$ denotes the homogeneous atomic fractions in the absence of an electric field, *i.e.* if $\varphi_{\mathrm{L}} = \varphi_{\mathrm{R}}$. Note that the potential Φ and the atomic fractions are independent of each other in the bulk region. This fact is due to the assumed incompressibility, and because we have ignored chemical reactions.

(5) Finally we consider the behavior of the mechanical stress, which is represented by the component Σ_{11} in our 1D treatment. The stress Σ_{11} appears in the momentum balance (eqn (2)) after elimination of the free charge density by means of the Poisson equation. A simple calculation yields the following alternative form of the momentum balance (eqn (2)):

$$\partial_x \Sigma_{11} = 0 \ \text{ with } \ \Sigma_{11} = -p + \tfrac{1}{2}\varepsilon_0(1+\chi)(\partial_x \varphi)^2. \tag{19}$$

We conclude that the stress consists of the elastic pressure p and the so called Maxwell stress due to the electric field. Eqn $(19)_1$ implies that Σ_{11} must be a constant in the whole domain. Its value is given by the boundary condition $\Sigma_{11}(x = L) = -p_0$. On the other hand Fig. 1 shows large variations of $\nabla\varphi$ in the two boundary layers. Obviously these variations are counterbalanced by the elastic pressure to obtain a constant total stress Σ_{11}. That pressure can be read off from Fig. 3. Because p appears in the chemical potentials, it has an extremely large influence on the solution and cannot be ignored.

2.3 Survey of the literature

In 1889 and 1890 W. Nernst and M. Planck published the papers on electrolytes.[2–4] These papers form the basis of what came to be called the Nernst–Planck model, which consists of constitutive equations for the diffusion fluxes. For a liquid mixture with N constituents the Nernst–Planck law reads in our notation

$$\boldsymbol{J}_\alpha = -M_\alpha^{\mathrm{NP}}(k\nabla n_\alpha + z_\alpha e_0 n_\alpha \nabla\varphi) \ \text{ for } \ \alpha \in \{1,\ldots,N\}. \tag{20}$$

We have introduced here the Nernst–Planck mobilities $M_\alpha^{\mathrm{NP}} > 0$. They are often considered to be the same constant for each constituent. Nowadays the Nernst–Planck flux is still used by many authors, presumably because it is the only model that is exploited in the popular textbook by Newman and Thomas-Alyea.[5]

In those days when Nernst and Planck formulated their model, non-equilibrium thermodynamics was not properly developed. In particular the authors gave no explicit definition of the diffusion flux in terms of the corresponding velocities of

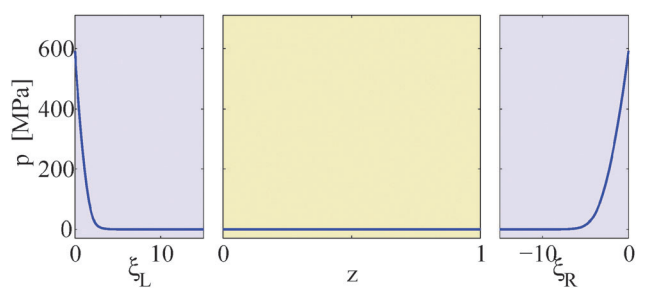

Fig. 3 Pressure p in the boundary regions and the bulk for the situation of Fig. 1.

the constituents. Moreover the role of the barycentric velocity was not clear. For this reason Planck may have overlooked the fact that there are only $N-1$ independent diffusion fluxes.

Modern non-equilibrium thermodynamics started in 1940. A few years later the correct driving force for the $N-1$ independent diffusion fluxes could be identified without any doubt, see the monographs by deGroot–Mazur[6] and Müller,[7] *viz.*

$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\left(\nabla\frac{\mu_\beta-\mu_N}{T}+\frac{e_0}{T}\left(\frac{z_\beta}{m_\beta}-\frac{z_N}{m_N}\right)\nabla\varphi\right) \quad \text{for } \alpha\in\{1,\dots,N-1\}. \tag{21}$$

Note that the temperature appears under the gradient in the first term and in front of the gradient in the second term. However, this is not important here because we exclusively consider isothermal processes.

Next we give the necessary assumptions so that the Nernst–Planck flux (eqn (20)) becomes a special case of the thermodynamically correct diffusion law (eqn (21)): (i) the constituent $\alpha = N$ is the neutral solvent, *i.e.* $z_N = 0$. (ii) The total number density n of the mixture is constant. (iii) The chemical potential μ_N is constant, so that $\nabla\mu_N = 0$. (iv) The chemical potentials of the other constituents are given by $\mu_\alpha = kT/m_\alpha \ln(n_\alpha/n) + \mu_\alpha^{\mathrm{R}}$, where μ_α^{R} is a constant. (v) The mobility matrix in eqn (21) is diagonal with entries proportional to the number densities n_α, so that $M_{\alpha\beta} = 0$ for $\alpha \neq \beta$ and $M_{\alpha\alpha} = M_\alpha^{\mathrm{NP}} T m_\alpha{}^2 n_\alpha$.

Under these assumptions the Nernst–Plank law for $\alpha \in \{1,2,\dots,N-1\}$ turns out to be a special case of the correct law (eqn (21)). However, the Nernst–Planck law for $\boldsymbol{J}_N$ is still wrong because we must have $\boldsymbol{J}_N = -\sum_{\alpha=1}^{N-1}\boldsymbol{J}_\alpha$.

Let us now discuss the status of the five assumptions. If there is a neutral solvent, the assumption (i) turns into an agreement. Assumption (ii) is simply a possible characterization of a liquid mixture. The assumption (iii) is valid for stationary processes with $\boldsymbol{J}_\alpha = 0$, *i.e.* for equilibria. For this special case, (iii) can be derived from a combination of the momentum balance and the diffusion law, see eqn (68) and (69). However, if the diffusion fluxes are not zero, the assumption (iii) is false. Moreover, the combination of assumption (iii) and assumption (iv) leads to a contradiction because it implies n_N = constant, leading to an over-determined system of equations. This will not happen in our model, where the chemical potentials depend on the atomic fractions n_α/n and on the pressure p. Thus assumption (iv) is not possible. The assumption (v) on the mobility matrix perfectly approximates many electrolytes.

We conclude that assumption (iv) and the constitutive law (eqn (20)) for $\boldsymbol{J}_N$ make the Nernst–Planck law inapplicable. Moreover, recall that assumption (iii) is only possible in the special case $\boldsymbol{J}_\alpha = 0$.

There is a large community interested in the coupled system of the Nernst–Planck model and the Navier–Stokes equations. Obviously many people in this community immediately recognized the deficiency of the Nernst–Planck law (eqn (20)) concerning $\boldsymbol{J}_N$. For example, see ref. 8 and 9. In order to guarantee the side condition $\sum_{\alpha=1}^{N}\boldsymbol{J}_\alpha = 0$, T. Roubíček introduced in ref. 8 two new mobilities M_1 and M_2, that are independent of the constituents, and modified the Nernst–Planck law (eqn (20)) according to

$$\boldsymbol{J}_\alpha = -M_1\nabla\frac{n_\alpha}{n} - M_2\left(z_\alpha e_0 n_\alpha - n^{\mathrm{F}}\right)\nabla\varphi \quad \text{for } \alpha\in\{1,\dots,N\}. \tag{22}$$

The side condition is now satisfied. However, the modification (eqn (22)) of the Nernst–Planck law violates the 2nd law of thermodynamics because the driving force is not a special case of the correct driving force in eqn (21). This fact is missed in ref. 9.

We also mention here I. Rubinstein's monograph on *Electro-Diffusion of Ions*,[10] containing a bundle of most interesting physical examples and mathematical methods. However, the basis of the monograph is the unmodified Nernst–Planck law with N diffusion equations that are coupled to the incompressible Navier–Stokes equations. The necessity to modify the Nernst–Planck law in this context is ignored. The same system of equations is mathematically studied in the thesis *Modeling, Analysis, and Numerics in Electrohydrodynamics* by M. Schmuck.[11] Here the objective is to transfer the Nernst–Planck–Poisson–Navier–Stokes system to the discrete setting.

M. Z. Bazant *et al.*[12] study the time dependent behavior of a binary electrolyte with very interesting boundary conditions. The analysis completely relies on the Nernst–Planck law with two independent diffusion equations for two constituents. The properties of the solvent are not considered here. Recall, we found out that the solvent must be taken into account.

M. S. Kilic *et al.*[13] leave the Nernst–Planck setting and propose a modified free energy function to model boundary layers in non-dilute electrolytes. The paper contains an excellent asymptotical treatment of the boundary layers. In contrast to our study the authors identify a different physical origin of the boundary layers.

In 2011 M. Z. Bazant *et al.* present a completely new electrolyte model that does not rely on the Nernst–Planck law.[14] The authors propose that higher gradients of the electric potential should be included. In particular they propose a modified Poisson equation which now contains spatial derivatives of fourth order. The exploitation of the equations is based on asymptotic analysis which is very carefully described. We agree with the authors that higher gradients are necessary, see eqn (13). However, in the current study we will show that their introduction can be done within the fully classical setting if the coupling between diffusion and the momentum balance is properly taken into account.

M. Landstorfer *et al.*[15] study the properties of solid electrolytes. They take vacancies into account and thus obtain a Fermi-type representation of the atomic fraction. The classical Nernst–Planck law is correspondingly modified. Likewise as in ref. 12 the authors introduce Robin boundary conditions for the electric potential.

A. Latz and J. Zausch[16] introduce thermodynamic models for all components of lithium-ion batteries. Concerning the electrolyte they exclusively consider the case of local charge neutrality. For this reason the electrolyte model of Latz and Zausch is not capable of predicting the open circuit voltage: in equilibrium their model only allows a constant electric potential in the whole electrolyte. In our study we identify two facts for that shortcoming: (1) the assumption of local electro-neutrality which only holds far away from the boundaries and (2) disregarding of the coupling between mechanics and diffusion.

The seminal paper by H. Gajewski and K. Gröger[17] started a series of mathematical treatments of reaction–diffusion systems whose diffusional part uses the Nernst–Planck law. In the context of semi-conductor device simulations the Nernst–Planck–Poisson setting with chemical reactions is called the van Roosbroeck model. The mathematical treatment of our system in terms of Gajewski and Gröger is already started.

3 The electrolyte model

We consider a liquid mixture consisting of N constituents A_1, A_2,..., A_N indexed by $\alpha \in \{1, 2,\ldots, N\}$. The constituents have (atomic) masses $(m_\alpha)_{\alpha\in\{1,2,\ldots,N\}}$ and may be carrier of charges $(z_\alpha e_0)_{\alpha\in\{1,2,\ldots,N\}}$. The constants e_0 and z_α are the elementary charge and the charge numbers, respectively. In the following we will always substitute $z_\alpha e_0$ by z_α.

The constituent with the index N is the neutral solvent, *i.e.* $z_N = 0$. The solvent is polarizable by an electric field. We describe this phenomenon by a simple law that assumes proportionality between polarization and the local electric field with a constant dielectric susceptibility.

A further phenomenon, magnetization, is ignored here. Dissociation reactions are also ignored, *i.e.* we assume mass conservation laws for the neutral as well as for the charged species. We only consider isothermal processes, *i.e.* the temperature T will not change. Nevertheless, the temperature appears in the equations, but only as a constant parameter. Furthermore we neglect the viscosity of the mixture.

Basic quantities

The mixture occupies a region $\Omega \subset \mathbb{R}^3$. At any time $t \geq 0$, the thermodynamic state of Ω is described by the number densities $(n_\alpha)_{\alpha\in\{1,2,\ldots,N\}}$, the velocities $(\boldsymbol{v}_\alpha)_{\alpha\in\{1,2,\ldots,N\}}$ of the constituents, the temperature T and by the local electric field $\boldsymbol{E}$. The introduced quantities may be functions of time $t \geq 0$ and space $x = (x^1, x^2, x^3) \in \Omega$.

Multiplication of the number densities by the atomic masses m_α gives the partial mass densities

$$\rho_\alpha = m_\alpha n_\alpha. \tag{23}$$

The mass density of the mixture and the barycentric velocity are defined by

$$\rho = \sum_{\alpha=1}^{N} \rho_\alpha, \quad \boldsymbol{v} = \frac{1}{\rho}\sum_{\alpha=1}^{N} \rho_\alpha \boldsymbol{v}_\alpha. \tag{24}$$

The non-convective mass flux of constituent A_α is defined by

$$\boldsymbol{J}_\alpha = \rho_\alpha(\boldsymbol{v}_\alpha - \boldsymbol{v}). \tag{25}$$

Note that the definitions (24) and (25) imply the identity

$$\sum_{\alpha=1}^{N} \boldsymbol{J}_\alpha = 0. \tag{26}$$

Total free charge density and total free electric current of the mixture are given by

$$n^{\mathrm{F}} = \sum_{\alpha=1}^{N} z_\alpha n_\alpha \quad \text{and} \quad j^{\mathrm{F}} = \sum_{\alpha=1}^{N} z_\alpha n_\alpha v_\alpha. \tag{27}$$

Besides free charge densities and free electric currents there are charge densities and currents due to polarization. The application of Maxwell's theory to continuous matter shows that these quantities may be represented by the polarization:[7]

$$n^{\mathrm{P}} = -\mathrm{div}\boldsymbol{P}, \quad \boldsymbol{j}^{\mathrm{P}} = \frac{\partial \boldsymbol{P}}{\partial t} + \mathrm{curl}(\boldsymbol{P} \times \boldsymbol{v}). \tag{28}$$

The polarization vector $\boldsymbol{P}$ encodes microscopic charges and currents that are not resolved on the macroscopic scale, for example atomic dipoles.

Total electric charge density and total electric current are given by

$$n^{\mathrm{e}} = n^{\mathrm{F}} + n^{\mathrm{P}} \quad \text{and} \quad \boldsymbol{j}^{\mathrm{e}} = \boldsymbol{j}^{\mathrm{F}} + \boldsymbol{j}^{\mathrm{P}}. \tag{29}$$

Finally, we introduce the total number density of the mixture and the atomic fractions of each constituent

$$n = \sum_{\alpha=1}^{N} n_\alpha, \quad y_\alpha = \frac{n_\alpha}{n} \text{ with } \sum_{\alpha=1}^{N} y_\alpha = 1. \tag{30}$$

Equations of balance for matter in the bulk

The coupled system of equations for the basic variables rely on partial equations of balance, *i.e.* on the conservation laws for the mass of the constituents and the balance equations for the momentum of the mixture. In the bulk those laws may be written as

$$\partial_t \rho_\alpha + \mathrm{div}(\rho_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha) = 0 \quad \text{for } \alpha \in \{1,\ldots,N\}, \tag{31}$$

$$\partial_t \rho \boldsymbol{v} + \mathrm{div}(\rho \boldsymbol{v} \otimes \boldsymbol{v} - \boldsymbol{\sigma}) = \rho \boldsymbol{b} + \boldsymbol{k}. \tag{32}$$

The quantity $\boldsymbol{\sigma}$ is the stress tensor. The force density is decomposed into two different types: $\rho\boldsymbol{b}$ – force density due to gravitation and inertia, $\boldsymbol{k}$ – Lorentz force density due to electromagnetic fields. We assume here $\boldsymbol{b} = 0$ and without the magnetic contribution the (static) Lorentz force is given by

$$\boldsymbol{k} = n^{\mathrm{e}}\boldsymbol{E}. \tag{33}$$

Equations for the electric field in the bulk

We consider quasi-static electric fields only, so that the Maxwell equations in the bulk reduce to the Poisson equation:

$$\varepsilon_0 \,\mathrm{div}(\boldsymbol{E}) = n^{\mathrm{e}}, \quad \boldsymbol{E} = -\nabla\varphi. \tag{34}$$

Constitutive model, Part 1: general setting

We consider a non-viscous and non-reacting mixture. Furthermore we ignore the Debye interaction between the charged constituents and do not consider temperature variations. We thus exclusively aim to describe diffusion and volume changes under isothermal conditions.

The constitutive model relies on a free energy function of the general form

$$\rho\psi = \rho\psi(T,\rho_1,\rho_2,\ldots,\rho_N, \boldsymbol{E}). \tag{35}$$

Based on the general function (eqn (35)), the axioms of the 2nd law of thermodynamics give rise to the following constitutive model:[6,7]

1. Chemical potentials and polarization:

$$\mu_\alpha = \frac{\partial\rho\psi}{\partial\rho_\alpha},\ \boldsymbol{P} = -\frac{\partial\rho\psi}{\partial\boldsymbol{E}}. \tag{36}$$

2. Representation of the stress:

$$\boldsymbol{\sigma} = \left(\rho\psi - \sum_{\alpha=1}^{N}\rho_\alpha\mu_\alpha\right)\mathbf{1} + \boldsymbol{E}\otimes\boldsymbol{P}, \tag{37}$$

where $\mathbf{1}$ denotes the unit matrix.

3. Representation and sign of the entropy production:

$$\xi = -\sum_{\alpha=1}^{N}\boldsymbol{J}_\alpha\cdot\left(\nabla\left(\frac{\mu_\alpha}{T}\right) - \frac{1}{T}\frac{z_\alpha}{m_\alpha}\boldsymbol{E}\right). \tag{38}$$

The entropy production ξ must be non-negative for every solution of the balance equations, $\xi \geq 0$. Equilibrium is a solution of the balance equations with $\xi = 0$.

The representation of ξ is important because it allows us to formulate a constitutive function for the diffusion flux that guarantees $\xi \geq 0$. In this case we say that the diffusion fluxes are compatible with the 2nd law of thermodynamics. The simplest choice of constitutive functions for $(N-1)$ diffusion fluxes $(\boldsymbol{J}_\alpha)_{\alpha\in\{1,2,\ldots,N-1\}}$ are

$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N-1}M_{\alpha\beta}\left(\nabla\left(\frac{\mu_\beta-\mu_N}{T}\right) - \frac{1}{T}\left(\frac{z_\beta}{m_\beta}-\frac{z_N}{m_N}\right)\boldsymbol{E}\right) \tag{39}$$

$$\text{for } \alpha\in\{1,2,\ldots,N-1\}.$$

The kinetic matrix $M_{\alpha\beta}$ must be positive definite.

It is important to note that only $(N-1)$ diffusion fluxes are given by constitutive laws. Due to the side condition (eqn (26)), the flux $\boldsymbol{J}_N$ is expressed by the other $(N-1)$ fluxes according to $\boldsymbol{J}_N = -\sum_{\alpha=1}^{N-1}\boldsymbol{J}_\alpha$.

Constitutive model, Part 2: special constitutive model for the free energy density

The general constitutive laws become explicit functions of the variables if the free energy function (eqn (35)) and the kinetic matrix are given. We consider a free energy density of the following form

$$\rho\psi = \sum_{\alpha=1}^{N}\rho_\alpha\psi_\alpha^{\mathrm{R}} + \rho\psi_{\mathrm{M}} + \rho\psi_{\mathrm{E}} + \rho\psi_{\mathrm{P}}. \tag{40}$$

The index R indicates the reference states of the pure constituents and the other contributions are due to

(1) isotropic elastic deformation with a constant bulk modulus $K > 0$,

$$\rho\psi_{\mathrm{M}} = \left(K - p^{\mathrm{R}}\right)\left(1-\frac{n}{n^{\mathrm{R}}}\right) + K\frac{n}{n^{\mathrm{R}}}\ln\left(\frac{n}{n^{\mathrm{R}}}\right). \tag{41}$$

(2) entropy of mixing,

$$\rho\psi_{\mathrm{E}} = nkT\sum_{\alpha=1}^{N}y_\alpha\ln(y_\alpha). \tag{42}$$

(3) dielectric polarization with a constant susceptibility $\chi > 0$

$$\rho\psi_{\mathrm{P}} = -\frac{1}{2}\varepsilon_0\chi|\boldsymbol{E}|^2. \tag{43}$$

For simplicity we assume that bulk modulus K and susceptibility χ do not depend on the atomic fractions y_α.

Inserting the free energy density into the general formulas (36) and (37) yields explicit constitutive functions. The chemical potentials (eqn $(36)_1$) read

$$\mu_\alpha = g_\alpha + \frac{kT}{m_\alpha}\ln(y_\alpha) \tag{44}$$

with

$$g_\alpha = g_\alpha^{\mathrm{R}} + \frac{K}{m_\alpha n^{\mathrm{R}}}\ln\left(\frac{n}{n^{\mathrm{R}}}\right), \tag{45}$$

where g_α denotes the specific Gibbs energy of the pure constituent A_α. The reference value of g_α is defined as $g_\alpha^{\mathrm{R}} = \psi_\alpha^{\mathrm{R}} + p^{\mathrm{R}}/(m_\alpha n^{\mathrm{R}})$. From eqn $(36)_2$ we obtain the polarization

$$\boldsymbol{P} = \varepsilon_0\chi\boldsymbol{E}, \tag{46}$$

and the stress (eqn (37)) results as

$$\boldsymbol{\sigma} = -\left(p^{\mathrm{R}} + K\left(\frac{n}{n^{\mathrm{R}}}-1\right)\right)\mathbf{1} - \frac{1}{2}\varepsilon_0\chi|\boldsymbol{E}|^2\mathbf{1} + \varepsilon_0\chi\boldsymbol{E}\otimes\boldsymbol{E}. \tag{47}$$

Elastic stress

In order to extract the elastic part of the stress we insert in eqn (37) the condition $\boldsymbol{E} = 0$ and obtain

$$\sigma|_{\boldsymbol{E}=0} = -p\mathbf{1} \text{ with } p = \left(-\rho\psi + \sum_{\alpha=1}^{N}\rho_\alpha\mu_\alpha\right)\Bigg|_{\boldsymbol{E}=0} \tag{48}$$

where p is the elastic pressure. Its explicit representation follows from the constitutive assumptions (40)–(43):

$$p = p^{\mathrm{R}} + K\left(\frac{n}{n^{\mathrm{R}}}-1\right). \tag{49}$$

Maxwell stress

The electric force $\boldsymbol{k}$ can be written as the divergence of a quantity that is called Maxwell stress. By means of the Poisson equation we may write

$$\boldsymbol{k} = \varepsilon_0\,\mathrm{div}(\boldsymbol{E})\boldsymbol{E} = \mathrm{div}(\varepsilon_0(\boldsymbol{E}\otimes\boldsymbol{E} - \tfrac{1}{2}|\boldsymbol{E}|^2)\mathbf{1}). \tag{50}$$

Moving the divergence term to the left hand side of the momentum balance (eqn (32)) leads to

$$\partial_t\rho\boldsymbol{v} + \mathrm{div}(\rho\boldsymbol{v}\otimes\boldsymbol{v} - \boldsymbol{\Sigma}) = 0, \tag{51}$$

where the newly introduced total stress

$$\boldsymbol{\Sigma} := \boldsymbol{\sigma} + \varepsilon_0(\boldsymbol{E} \otimes \boldsymbol{E} - \tfrac{1}{2}|\boldsymbol{E}|^2\mathbf{1}) \tag{52}$$

consists of the Maxwell stress due to the electric field and the material stress $\boldsymbol{\sigma}$. The total stress $\boldsymbol{\Sigma}$ is important because it is continuous at a plane boundary at rest. Therefore the total stress must be used to formulate boundary conditions.

Finally, we insert the constitutive function for the material stress $\boldsymbol{\sigma}$ into the representation of $\boldsymbol{\Sigma}$. We obtain

$$\boldsymbol{\Sigma} = -(p + \tfrac{1}{2}\varepsilon_0(1+\chi)|\boldsymbol{E}|^2)\mathbf{1} + \varepsilon_0(1+\chi)\boldsymbol{E} \otimes \boldsymbol{E}. \tag{53}$$

Summary

We now summarize the complete new electrolyte model. It consists of the system

$$\partial_t \rho + \operatorname{div}(\rho \boldsymbol{v}) = 0 \tag{54}$$

$$\partial_t(m_\alpha n_\alpha) + \operatorname{div}(m_\alpha n_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha) = 0 \quad \text{for} \quad \alpha \in \{1,\ldots,N-1\}, \tag{55}$$

$$\partial_t \rho \boldsymbol{v} + \operatorname{div}(\rho \boldsymbol{v} \otimes \boldsymbol{v}) + \nabla p = -n^{\mathrm{F}} \nabla \varphi, \tag{56}$$

$$-\varepsilon_0(1+\chi)\Delta\varphi = n^{\mathrm{F}}. \tag{57}$$

The constitutive equations for the $N-1$ diffusion fluxes are given by

$$\boldsymbol{J}_\alpha = -\sum_{\beta=1}^{N-1} M_{\alpha\beta}\left(\nabla\frac{\mu_\beta - \mu_N}{T} + \frac{1}{T}\left(\frac{z_\beta}{m_\beta} - \frac{z_N}{m_N}\right)\nabla\varphi\right) \quad \text{for } \alpha \in \{1,\ldots,N-1\}. \tag{58}$$

For $\alpha \in \{1,\ldots,N\}$ we have the chemical potentials

$$\mu_\alpha = g_\alpha + \frac{kT}{m_\alpha}\ln(y_\alpha) \quad \text{with} \quad g_\alpha = g_\alpha^{\mathrm{R}} + \frac{K}{m_\alpha n^{\mathrm{R}}}\ln\left(\frac{n}{n^{\mathrm{R}}}\right) \tag{59}$$

and the elastic pressure

$$p = p^{\mathrm{R}} + K\left(\frac{n}{n^{\mathrm{R}}} - 1\right). \tag{60}$$

For completeness we write down the total electric current j^{e} consisting of a part due to the flow of free charges and a further part due to polarization

$$j^{\mathrm{e}} = \sum_{\alpha=1}^{N} \frac{z_\alpha}{m_\alpha}(\rho_\alpha \boldsymbol{v} + \boldsymbol{J}_\alpha) - \varepsilon_0\chi\left(\frac{\partial\nabla\varphi}{\partial t} + \operatorname{curl}(\nabla\varphi \times \boldsymbol{v})\right).$$

4 An equilibrium boundary problem in 1D

We consider in one space dimension an electrolytic solution consisting of 3 constituents: positively charged cations C, negatively charged anions A, and the neutral solvent S. The corresponding charges are $z_{\mathrm{C}} > 0$, $z_{\mathrm{A}} < 0$ and $z_{\mathrm{S}} = 0$. We only study equilibrium processes that are characterized by vanishing diffusion fluxes and vanishing barycentric velocity of the mixture:

$$\boldsymbol{J}_\alpha = 0 \quad \text{and} \quad \boldsymbol{v} = 0. \tag{61}$$

For $x \in [0, L]$ the models (54)–(60) reduce to the Poisson equation, the stationary momentum balance and two independent equations, which guarantee vanishing diffusion fluxes

$$-\varepsilon_0(1+\chi)\partial_{xx}\varphi = n^{\mathrm{F}}, \tag{62}$$

$$\partial_x p = -n^{\mathrm{F}}\partial_x\varphi, \tag{63}$$

$$\partial_x\left(\mu_{\mathrm{C}} - \mu_{\mathrm{S}} + \frac{z_{\mathrm{C}}}{m_{\mathrm{C}}}\varphi\right) = 0, \tag{64}$$

$$\partial_x\left(\mu_{\mathrm{A}} - \mu_{\mathrm{S}} + \frac{z_{\mathrm{A}}}{m_{\mathrm{A}}}\varphi\right) = 0. \tag{65}$$

Equilibria of this kind may be established by a high resistance voltage source between the electrodes and a prescribed boundary pressure. Thus we choose as boundary conditions

$$\varphi(x=0) = \varphi_{\mathrm{L}}, \quad \varphi(x=L) = \varphi_{\mathrm{R}}, \quad \Sigma_{11}(x=L) = -p_0. \tag{66}$$

The left boundary is fixed at $x = 0$. The location L of the right boundary is determined by p_0 and by the side condition of prescribed masses. A further side condition arises because we assume global charge neutrality. The two conditions read

$$\int_0^L \rho_\alpha \,\mathrm{d}x = M_\alpha \ \text{ for } \ \alpha \in \{\mathrm{C},\mathrm{A},\mathrm{S}\}, \quad \int_0^L n^{\mathrm{F}}\,\mathrm{d}x = 0. \tag{67}$$

Useful relation

In the isothermal case the model implies a simple relation between the gradients of the elastic pressure and the chemical potentials. The relation reads

$$\partial_x p = \sum_{\alpha=1}^{N} \rho_\alpha \partial_x \mu_\alpha \tag{68}$$

and is a simple consequence of eqn $(48)_2$ and $(36)_1$. Eqn (68) can also be written as

$$\partial_x p = \sum_{\alpha=1}^{N} \rho_\alpha \partial_x(\mu_\alpha - \mu_N) + \rho\partial_x\mu_N. \tag{69}$$

Here we substitute $\partial_x p$ by the momentum balance (63). Furthermore on the right hand side of eqn (69) we insert eqn (64) and (65). For the case at hand with three constituents, the result is

$$\partial_x \mu_{\mathrm{S}} = 0, \tag{70}$$

which is very plausible because the solvent is not a carrier of charge.

Dimensionless quantities

In order to express the model equations by dimensionless quantities we substitute as follows. The space coordinate is scaled by the total length, $x = Lz$ with $z \in [0,1]$. Furthermore we substitute

$$n \to n^{\mathrm{R}}n, \ \ p \to p^{\mathrm{R}}p, \ \ L \to L^{\mathrm{R}}L, \ \ z_\alpha \to e_0 z_\alpha, \ \ K \to p^{\mathrm{R}}K,$$

$$\Sigma_{11} \to p^{\mathrm{R}}\Sigma_{11}, \ n^{\mathrm{F}} \to n^{\mathrm{R}}e_0 n^{\mathrm{F}}, \ \ g_\alpha \to \frac{kT}{m_\alpha}g_\alpha, \ \ \mu_\alpha \to \frac{kT}{m_\alpha}\mu_\alpha, \ \ \varphi \to \frac{kT}{e_0}\varphi,$$

without indicating the corresponding dimensionless quantities.

Boundary problem in dimensionless quantities

Introduction of the dimensionless quantities into the relevant equations generates two positive constants, *viz.*

$$\lambda^2 = \frac{kT\varepsilon_0(1+\chi)}{e_0^2 n^{\mathrm{R}}(L^{\mathrm{R}})^2} \quad \text{and} \quad a^2 = \frac{p^{\mathrm{R}}}{n^{\mathrm{R}}kT}. \tag{71}$$

The transformed differential equations then read

$$\lambda^2\partial_{zz}\varphi = -L^2 n^{\mathrm{F}}, \tag{72}$$

$$a^2\partial_z p = -n^{\mathrm{F}}\partial_z\varphi, \tag{73}$$

$$\partial_z(\mu_{\mathrm{C}} + z_{\mathrm{C}}\varphi) = 0, \tag{74}$$

$$\partial_z(\mu_{\mathrm{A}} + z_{\mathrm{A}}\varphi) = 0. \tag{75}$$

Note, μ_{S} has disappeared in eqn (74) and (75) due to eqn (70).

These equations are supplemented by the representation of the charge density and by constitutive equations for pressure, chemical potentials, specific Gibbs free energies and total stress

$$n^{\mathrm{F}} = n(z_{\mathrm{C}}y_{\mathrm{C}} + z_{\mathrm{A}}y_{\mathrm{A}}), \tag{76}$$

$$p = 1 + K(n-1), \tag{77}$$

$$\mu_\alpha = g_\alpha + \ln(y_\alpha), \tag{78}$$

$$g_\alpha = g_\alpha^{\mathrm{R}} + a^2 K \ln\left(1 + \frac{1}{K}(p-1)\right), \tag{79}$$

$$\Sigma_{11} = -p + \frac{\lambda^2}{2a^2}L^2(\partial_z\varphi)^2. \tag{80}$$

The transformed boundary data are

$$\varphi(0) = \frac{e_0}{kT}\varphi_{\mathrm{L}}, \quad \varphi(1) = \frac{e_0}{kT}\varphi_{\mathrm{R}}, \quad \Sigma_{11}(1) = -\frac{p_0}{p_{\mathrm{R}}}. \tag{81}$$

Finally we write the transformed versions of mass conservation and global charge neutrality as

$$L\int_0^1 n y_\alpha \,\mathrm{d}z = \frac{M_\alpha}{m_\alpha n^{\mathrm{R}} L^{\mathrm{R}}}, \quad \alpha \in \{\mathrm{C},\mathrm{A},\mathrm{S}\}, \tag{82}$$

$$L\int_0^1 n(z_{\mathrm{C}}y_{\mathrm{C}} + z_{\mathrm{A}}y_{\mathrm{A}})\,\mathrm{d}z = 0. \tag{83}$$

The equations of this paragraph suggest to change the variables from φ, n_{C}, n_{A} and n_{S} to

$$\varphi,\ n,\ y_{\mathrm{C}},\ y_{\mathrm{A}}, \tag{84}$$

and the mole fraction y_{S} is calculated from

$$y_{\mathrm{S}} = 1 - y_{\mathrm{C}} - y_{\mathrm{A}}. \tag{85}$$

5 The incompressible limit

Incompressibility

There are various possibilities to introduce the notion of incompressibility. In this study we define incompressibility by the limit $K \to \infty$. The bulk modulus of liquids is often quite large and then the incompressible limit is a fairly well approximation.

Let us consider the constitutive law (eqn (77)) for the pressure. We do not expect that the pressure tends to infinity if we assume $K \to \infty$. Thus we must have $n \to 1$. In this case the product $K(n-1)$ becomes undetermined and the pressure cannot be calculated from eqn (77) anymore. However, we still have to satisfy the momentum balance (eqn (73)).

Many superficial treatments of this limiting case suggest that it reduces the number of variables. This impression is false! Note that the number of variables is not reduced, but instead of the variables (84) we now have as independent variables

$$\varphi,\ p,\ y_{\mathrm{C}},\ y_{\mathrm{A}}. \tag{86}$$

Exploitation of incompressibility

Note that the specific Gibbs energy (eqn (79)) becomes

$$g_\alpha \to g_\alpha^{\mathrm{R}} + a^2(p-1) \quad \text{for} \quad K \to \infty. \tag{87}$$

We insert this result and $n = 1$ into the constitutive laws (76)–(79), and afterwards we consider the system (72)–(75). Some simple rearrangements of terms lead to

$$\lambda^2\partial_{zz}\varphi = -L^2(z_{\mathrm{C}}y_{\mathrm{C}} + z_{\mathrm{A}}y_{\mathrm{A}}), \tag{88}$$

$$\partial_z(\ln(y_{\mathrm{C}}) + z_{\mathrm{C}}\varphi + \tfrac{1}{2}\lambda^2(\partial_z\varphi)^2) = 0, \tag{89}$$

$$\partial_z(\ln(y_{\mathrm{A}}) + z_{\mathrm{A}}\varphi + \tfrac{1}{2}\lambda^2(\partial_z\varphi)^2) = 0. \tag{90}$$

Apparently this system is decoupled from the momentum law (eqn (73)), which now is used to determine the pressure after the system (88)–(90) has been solved for φ, y_{C}, y_{A} and $y_{\mathrm{S}} = 1 - y_{\mathrm{C}} - y_{\mathrm{A}}$.

The boundary data for φ in the incompressible case are the same as before, *viz.*

$$\varphi(z=0) = \frac{e_0}{kT}\varphi_{\mathrm{L}}, \quad \varphi(z=1) = \frac{e_0}{kT}\varphi_{\mathrm{R}}, \tag{91}$$

but the constraints can now be written as

$$L\int_0^1 y_\alpha \,\mathrm{d}z = \bar{y}_\alpha, \quad \int_0^1 (z_{\mathrm{C}}y_{\mathrm{C}} + z_{\mathrm{A}}y_{\mathrm{A}})\,\mathrm{d}z = 0. \tag{92}$$

Here $\bar{y}_\alpha = M_\alpha/(m_\alpha n^{\mathrm{R}}L^{\mathrm{R}})$ is the atomic fraction of the homogeneous mixture in the reference state. Furthermore we have

$$L = 1 \tag{93}$$

in the incompressible limit. This follows from $n = 1$ and the normalizations $y_{\mathrm{C}} + y_{\mathrm{A}} + y_{\mathrm{S}} = 1$ and $\bar{y}_{\mathrm{C}} + \bar{y}_{\mathrm{A}} + \bar{y}_{\mathrm{S}} = 1$.

6 General properties of the solution

In preparation for the numerical solution of the boundary value problem (eqn (88)–(92)) we study at first various properties of the solution. In this section we start with general properties.

Representations of the atomic fractions

Integration of eqn (89) and (90) yields the atomic fraction y_{C} and y_{A} as functions of the potential and its derivative:

$$y_\alpha = c_\alpha \exp(-z_\alpha\varphi - \tfrac{1}{2}\lambda^2(\partial_z\varphi)^2) \quad \text{for} \quad \alpha \in \{\mathrm{C},\mathrm{A}\}. \tag{94}$$

Recall eqn (70), which gives $\partial_z \mu_S = 0$ in equilibrium. Here we insert eqn (78) into eqn (87). A subsequent exploitation yields

$$y_S = c_S \exp(-\tfrac{1}{2}\lambda^2(\partial_z\varphi)^2). \tag{95}$$

Thus with $z_S = 0$ the representation (94) is also valid for the solvent.

The positive integration constants c_α may be determined by the side conditions $(92)_1$. For $\alpha \in \{C,A,S\}$, we obtain

$$c_\alpha = \bar{y}_\alpha \left(\int_0^1 \exp\left(-z_\alpha \varphi - \frac{1}{2}\lambda^2 (\partial_z \varphi)^2 \right) \mathrm{d}z \right)^{-1}. \tag{96}$$

A first integral of the Poisson equation

The normalization condition $y_C + y_A + y_S = 1$ may be used to find a first integral of the Poisson equation. To this end we introduce here the representations (94) and (95) and directly obtain

$$1 = (c_C \exp(-z_C\varphi) + c_A \exp(-z_A\varphi) + c_S) \exp(-\tfrac{1}{2}\lambda^2(\partial_z\varphi)^2). \tag{97}$$

This can also be written as

$$\tfrac{1}{2}\lambda^2(\partial_z\varphi)^2 = \ln(c_S + c_C \exp(-z_C\varphi) + c_A \exp(-z_A\varphi)). \tag{98}$$

The behavior of $\partial_z\varphi$ at the boundaries and consequences

Let us exploit the condition $(92)_2$ of global charge neutrality by inserting the Poisson equation:

$$\begin{aligned} 0 &= \int_0^1 (z_C y_C + z_A y_A)\,\mathrm{d}z = -\lambda^2 \int_0^1 \partial_{zz}\varphi \,\mathrm{d}z \\ &= \lambda^2(\partial_z\varphi(0) - \partial_z\varphi(1)). \end{aligned} \tag{99}$$

Thus the slopes of φ at $z = 0$ and $z = 1$ must be equal.

This result is now used in eqn (98) at $z = 0$ and $z = 1$:

$$\frac{\lambda^2}{2}(\partial_z\varphi(0))^2 = \ln(c_S + c_C \exp(-z_C\varphi_L) + c_A \exp(-z_A\varphi_L)),$$

$$\frac{\lambda^2}{2}(\partial_z\varphi(1))^2 = \ln(c_S + c_C \exp(-z_C\varphi_R) + c_A \exp(-z_A\varphi_R)).$$

We conclude that the arguments of the logarithmic function must be equal and obtain

$$c_C \exp(-z_C\varphi_L) + c_A \exp(-z_A\varphi_L) = c_C \exp(-z_C\varphi_R) + c_A \exp(-z_A\varphi_R). \tag{100}$$

After determination of the integration constants, this equation will later be used to derive an algebraic formula for the potential in the middle between the two boundaries.

7 Asymptotic solution of the boundary problem

We proceed to study properties of the solution of the boundary problem (88)–(92). In this section we apply the methods of asymptotic analysis. A detailed description of the method of asymptotic analysis can be found in ref. 18.

Motivations and strategy

Our problem contains the extremely small parameter λ. If we were to set $\lambda = 0$ as an overall approximation in $z \in [0,1]$, only the constant solution will exist. In this case no solution exists at all. In particular, a constant potential φ cannot satisfy the boundary data (eqn (91)). Thus we expect that the solution of the problem generates boundary layers in the vicinity of $z = 0$ and $z = 1$, respectively. Problems of that kind may be treated by the method of formal asymptotic analysis that will be introduced next.

Decomposition of the domain

In order to describe a solution that may include boundary layers we decompose the interval [0,1] in the boundary regions L and R and in the bulk region B as it is indicated in Fig. 1. Correspondingly we seek for different solutions in the three regions. The bulk solution is called outer solution while the solutions in L and R are called inner solutions.

Moreover, Fig. 1 indicates two shaded regions where we have overlapping of L and B and of R and B, respectively. Here we expect matching of outer and inner solutions.

Expansions of outer and inner solutions

We assume that the solutions $\varphi^\lambda(x)$ and y_α^λ of the boundary problem can be expanded in series with respect to the small parameter λ.

In the bulk region B we write

$$\varphi^\lambda(z) = \varphi^0(z) + \lambda\varphi^1(z) + \mathcal{O}(\lambda^2), \tag{101}$$

$$y_\alpha^\lambda(z) = y_\alpha^0(z) + \lambda y_\alpha^1(z) + \mathcal{O}(\lambda^2). \tag{102}$$

In the boundary layers L and R, respectively, we introduce a new coordinate according to

$$z = \lambda\xi \quad \text{for } z \in \mathrm{L} \quad \text{and} \quad z = 1 + \lambda\xi \quad \text{for } z \in \mathrm{R}. \tag{103}$$

In L and R we define inner solutions by

$$\tilde{\varphi}_L^\lambda(\xi) = \varphi_L^\lambda(\lambda\xi), \quad \tilde{y}_{\alpha,L}^\lambda(\xi) = y_\alpha^\lambda(1 + \lambda\xi), \tag{104}$$

$$\tilde{\varphi}_R^\lambda(\xi) = \varphi_R^\lambda(\lambda\xi), \quad \tilde{y}_{\alpha,R}^\lambda(\xi) = y_\alpha^\lambda(1 + \lambda\xi). \tag{105}$$

Likewise as in the bulk region we assume expansions of the inner solutions and write

$$\tilde{\varphi}_L^\lambda(\xi) = \tilde{\varphi}_L^0(\xi) + \lambda\tilde{\varphi}_L^1(\xi) + \mathcal{O}(\lambda^2), \tag{106}$$

$$\tilde{y}_{\alpha,L}^\lambda(\xi) = \tilde{y}_{\alpha,L}^0(\xi) + \lambda\tilde{y}_{\alpha,L}^1(\xi) + \mathcal{O}(\lambda^2), \tag{107}$$

$$\tilde{\varphi}_R^\lambda(\xi) = \tilde{\varphi}_R^0(\xi) + \lambda\tilde{\varphi}_R^1(\xi) + \mathcal{O}(\lambda^2), \tag{108}$$

$$\tilde{y}_{\alpha,R}^\lambda(\xi) = \tilde{y}_{\alpha,R}^0(\xi) + \lambda\tilde{y}_{\alpha,R}^1(\xi) + \mathcal{O}(\lambda^2). \tag{109}$$

Boundary and matching conditions

The solution of the boundary problem in the three regions requires several conditions that will be given now. In this study it is sufficient to consider only those conditions involving the leading order terms.

Obviously we have to use the inner solutions to accommodate the boundary data (eqn (91)). We set

$$\tilde{\varphi}_L^0(0) = \frac{e_0}{kT}\varphi_L, \quad \tilde{\varphi}_R^0(0) = \frac{e_0}{kT}\varphi_R. \tag{110}$$

Further conditions result from the matching procedure in the overlap regions. We have

$$\lim_{\xi\to+\infty}\tilde{\varphi}^0_{\mathrm{L}}(\xi)=\varphi^0(z=0), \tag{111}$$

$$\lim_{\xi\to-\infty}\tilde{\varphi}^0_{\mathrm{R}}(\xi)=\varphi^0(z=1), \tag{112}$$

and for the derivatives

$$\lim_{\xi\to+\infty}\partial_\xi\tilde{\varphi}^0_{\mathrm{L}}(\xi)=0,\ \lim_{\xi\to-\infty}\partial_\xi\tilde{\varphi}^0_{\mathrm{R}}(\xi)=0. \tag{113}$$

The values on the right hand sides of eqn (111) and (112) are not known *a priori*; they must result from the outer solution.

In an analogous manner we have

$$\lim_{\xi\to+\infty}\tilde{y}^0_{\alpha,\mathrm{L}}(\xi)=y^0_\alpha(z=0), \tag{114}$$

$$\lim_{\xi\to-\infty}\tilde{y}^0_{\alpha,\mathrm{L}}(\xi)=y^0_\alpha(z=1). \tag{115}$$

Likewise the data for $y^0_\alpha(0)$ and $y^0_\alpha(1)$ must result from the outer solution.

Due to the global charge neutrality we obtain a further condition, *viz.* the inner version of eqn (99):

$$\partial_\xi\tilde{\varphi}^0_{\mathrm{L}}(0)=\partial_\xi\tilde{\varphi}^0_{\mathrm{R}}(0). \tag{116}$$

Properties of the solution in the bulk region

We introduce the outer expansion in the Poisson equation (eqn (88)) and obtain

$$z_{\mathrm{A}}y^0_{\mathrm{A}}+z_{\mathrm{C}}y^0_{\mathrm{C}}=0\quad\Rightarrow y^0_{\mathrm{A}}=-\frac{z_{\mathrm{C}}}{z_{\mathrm{A}}}y^0_{\mathrm{C}}. \tag{117}$$

From eqn (95) we conclude that y^0_{S} is a constant in the leading order. Due to eqn $(117)_2$ and $y_{\mathrm{C}}+y_{\mathrm{A}}+y_{\mathrm{S}}=1$ the other atomic fractions y^0_{C} and y^0_{A} also must be constants.

From eqn (94)–(96) we obtain in the leading order

$$y^0_\alpha=c^0_\alpha\exp(-z_\alpha\varphi^0)\quad\text{for}\quad\alpha\in\{\mathrm{C,A,S}\}. \tag{118}$$

with

$$c^0_\alpha=\bar{y}_\alpha\left(\int_0^1\exp\left(-z_\alpha\varphi^0\right)\mathrm{d}z\right)^{-1}. \tag{119}$$

Thus according to eqn (118) the potential φ^0 must also be a constant in the bulk region. We write

$$\varphi^0=\Phi. \tag{120}$$

The integration constants (119) and the atomic fractions (118) now simplify to

$$c^0_\alpha=\bar{y}_\alpha\exp(z_\alpha\Phi)\quad\text{and}\quad y^0_\alpha=\bar{y}_\alpha. \tag{121}$$

Properties of the solution in the boundary layers

In the inner coordinate ξ the Poisson equation becomes in the boundary layers L and R, respectively,

$$\partial_{\xi\xi}\tilde{\varphi}^0_{\mathrm{L/R}}=-z_{\mathrm{C}}\tilde{y}^0_{\mathrm{C,L/R}}-z_{\mathrm{A}}\tilde{y}^0_{\mathrm{A,L/R}}. \tag{122}$$

Accordingly the representations (94) and (95) may be written as

$$\tilde{y}^0_{\alpha,\mathrm{L}}=c^0_\alpha\exp(-z_\alpha\tilde{\varphi}^0_{\mathrm{L}}-\tfrac{1}{2}(\partial_\xi\tilde{\varphi}^0_{\mathrm{L}})^2), \tag{123}$$

$$\tilde{y}^0_{\alpha,\mathrm{R}}=c^0_\alpha\exp(-z_\alpha\tilde{\varphi}^0_{\mathrm{R}}-\tfrac{1}{2}(\partial_\xi\tilde{\varphi}^0_{\mathrm{R}})^2), \tag{124}$$

where $\alpha\in\{\mathrm{C,A,S}\}$. Finally we determine the plateau value of the potential in the bulk region, which is denoted by Φ. To this end we start with eqn (100), which we write in inner coordinates to obtain in the leading order

$$\begin{aligned}&y^0_{\mathrm{C}}\exp(-z_{\mathrm{C}}(\tilde{\varphi}^0_{\mathrm{L}}-\Phi))+y^0_{\mathrm{A}}\exp(-z_{\mathrm{A}}(\tilde{\varphi}^0_{\mathrm{L}}-\Phi))\\&\quad=y^0_{\mathrm{C}}\exp(-z_{\mathrm{C}}(\tilde{\varphi}^0_{\mathrm{R}}-\Phi))+y^0_{\mathrm{A}}\exp(-z_{\mathrm{A}}(\tilde{\varphi}^0_{\mathrm{R}}-\Phi))\end{aligned} \tag{125}$$

Here we have used the representation (121) of the integration constants. Solving eqn (125) for Φ and using eqn (117) to eliminate the atomic fractions yield

$$\Phi=\frac{e_0}{kT}\varphi_{\mathrm{R}}+\frac{1}{z_{\mathrm{A}}-z_{\mathrm{C}}}\ln\left(\frac{z_{\mathrm{A}}}{z_{\mathrm{C}}}\frac{1-\exp\left(\frac{e_0}{kT}z_{\mathrm{C}}(\varphi_{\mathrm{R}}-\varphi_{\mathrm{L}})\right)}{1-\exp\left(\frac{e_0}{kT}z_{\mathrm{A}}(\varphi_{\mathrm{R}}-\varphi_{\mathrm{L}})\right)}\right). \tag{126}$$

8 Numerical solution in the boundary layers

To determine the spacial profile of the leading order quantities $\tilde{\varphi}^0$, $\tilde{y}^0_{\mathrm{C}}$, $\tilde{y}^0_{\mathrm{A}}$ in the boundary layers, the governing differential equations have to be solved numerically. This requires to cut off the domains L and R such that $\xi\in(0,H)$ in L and $\xi\in(-H,0)$ in R for some finite length $H>0$. In the rest of this section we will skip the superscript 0.

From eqn (89) and (90) we derive for $\alpha\in\{\mathrm{A,C}\}$

$$0=\tilde{y}_\alpha(\partial_\xi\ln(\tilde{y}_\alpha)+z_\alpha\partial_\xi\tilde{\varphi}+\tfrac{1}{2}\partial_\xi(\partial_\xi\tilde{\varphi})^2)=\partial_\xi\tilde{y}_\alpha+\tilde{y}_\alpha\partial_\xi\tilde{\varphi}(z_\alpha+\partial_{\xi\xi}\tilde{\varphi}). \tag{127}$$

Together with the Poisson equation (eqn (122)) we get in L and in R the system of equations

$$\partial_{\xi\xi}\tilde{\varphi}+z_{\mathrm{C}}\tilde{y}_{\mathrm{C}}+z_{\mathrm{A}}\tilde{y}_{\mathrm{A}}=0, \tag{128}$$

$$\partial_\xi\tilde{y}_{\mathrm{C}}+\tilde{y}_{\mathrm{C}}\partial_\xi\tilde{\varphi}(z_{\mathrm{C}}-z_{\mathrm{C}}\tilde{y}_{\mathrm{C}}-z_{\mathrm{A}}\tilde{y}_{\mathrm{A}})=0, \tag{129}$$

$$\partial_\xi\tilde{y}_{\mathrm{A}}+\tilde{y}_{\mathrm{A}}\partial_\xi\tilde{\varphi}(z_{\mathrm{A}}-z_{\mathrm{C}}\tilde{y}_{\mathrm{C}}-z_{\mathrm{A}}\tilde{y}_{\mathrm{A}})=0. \tag{130}$$

The boundary values for $\tilde{\varphi}$ at $\xi=0$ are given by eqn (110), *i.e.*

$$\tilde{\varphi}_{\mathrm{L}}(0)=\frac{e_0}{kT}\varphi_{\mathrm{L}},\ \ \tilde{\varphi}_{\mathrm{R}}(0)=\frac{e_0}{kT}\varphi_{\mathrm{R}}. \tag{131}$$

At $\xi=\pm H$, we could prescribe $\tilde{\varphi}_{\mathrm{L}}(H)=\Phi=\tilde{\varphi}_{\mathrm{R}}(-H)$ according to eqn (126), but then we loose control over the derivatives of $\tilde{\varphi}$ that should vanish for $\xi\to\infty$. Instead, to approximate the boundary conditions (111) and (113), we enforce transmission conditions, *i.e.*

$$\tilde{\varphi}_{\mathrm{L}}(H)=\tilde{\varphi}_{\mathrm{R}}(-H)\quad\text{and}\quad\partial_\xi\tilde{\varphi}_{\mathrm{L}}(H)=\partial_\xi\tilde{\varphi}_{\mathrm{R}}(-H). \tag{132}$$

For the atomic fraction we have

$$\tilde{y}_{\alpha,\mathrm{L}}(H)=\tilde{y}_\alpha=\tilde{y}_{\alpha,\mathrm{R}}(-H)\quad\text{for}\quad\alpha\in\{\mathrm{C,A}\}. \tag{133}$$

We subdivide the domains L and R with an equidistant grid with step size $h>0$ and approximate the solutions with

continuous piecewise affine functions, *i.e.* $P1$-finite element functions. Then, spacial finite element discretization with mass lumping is equivalent to application of finite differences. In R, where we have to solve initial value problems for $\tilde{y}_\alpha$, the derivative is approximated by a backward difference. In L, we use forward differences since a final value is prescribed. The coupled nonlinear system is solved by a fixed point iteration with a damping factor $0 < w \le 1$.

Algorithm: given an initial guess $\tilde{\varphi}^0$, $\tilde{y}_C^0$ and $\tilde{y}_A^0$, for $j = 0, 1, 2 \ldots$, do

(1) Compute

$$\tilde{n}^{F,j} = z_C \tilde{y}_C^j + z_A \tilde{y}_A^j \quad \text{in L and R},$$

$$\tilde{m}^j = \frac{1}{2H}\left(\int_0^H \tilde{n}_L^{F,j}\,d\xi + \int_{-H}^0 \tilde{n}_R^{F,j}\,d\xi\right).$$

(2) Solve

$$-\partial_{\xi\xi}\tilde{\varphi}^{j+1/2} = \tilde{n}^{F,j} - \tilde{m}^j$$

with boundary conditions according to eqn (131) and (132).

(3) For $\alpha \in \{A,C\}$ solve

$$\partial_\xi \tilde{y}_\alpha^{j+1/2} + \tilde{y}_\alpha^{j+1/2}\partial_\xi \tilde{\varphi}^j[z_\alpha - \tilde{n}^{F,j}] = 0$$

in L and R with condition (133) for final or initial values respectively.

(4) Set $\tilde{\varphi}^{j+1} = w\tilde{\varphi}^{j+1/2} + (1-w)\tilde{\varphi}^j$,
set $\tilde{y}_\alpha^{j+1} = w\tilde{y}_\alpha^{j+1/2} + (1-w)\tilde{y}_\alpha^j$ for $\alpha \in \{A,C\}$.

We consider a ternary mixture with $z_A = -2$, $z_C = 1$ and $z_S = 0$. Computations for a strongly diluted mixture with $\tilde{y}_A = 2 \times 10^{-5}$ and $\tilde{y}_C = 4 \times 10^{-5}$ were carried out with $H = 1000$, $h = 1/40$ and $w = 1/20$. We checked that the solutions do not depend significantly on the step size h. The numerical solutions show sharp boundary layers at $\xi = 0$ and approach a constant value for $\xi \to \pm H$ (Fig. 4). Note that there are also boundary layers in the concentration y_S of the neutral solvent, *cf.* Fig. 7. Moreover, the results confirm the prediction (126) for the height Φ of the plateau, see Fig. 5.

The numerical results also show that the plateau height Φ does not depend on the atomic fractions in the bulk. This is illustrated in Fig. 6 for less diluted electrolytes. If the atomic fractions of anions and cations in the bulk tend to zero, then the boundary layers become wider and the numerical solution requires a larger domain size H.

When larger potential differences are prescribed, one of the atomic fractions reaches the saturation level $y_\alpha = 1$, see Fig. 7. We remark that it is not necessary to enforce $0 \le y_\alpha \le 1$ explicitly during the iteration process.

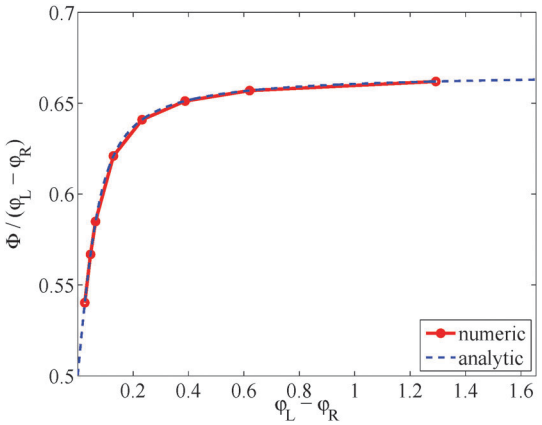

Fig. 5 Height Φ of the plateau depending on the applied potential difference. The numerical solution coincides with the nonlinear relation (126).

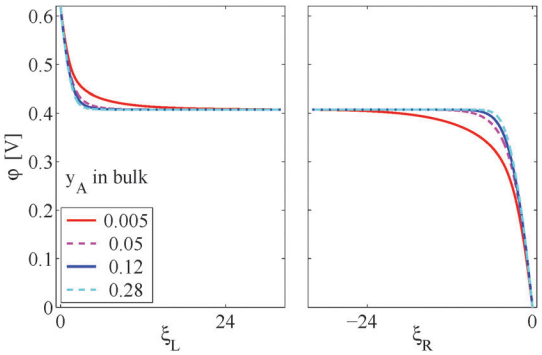

Fig. 6 Potential φ in the boundary regions for $\varphi_L - \varphi_R = 0.62$ V and different atomic fractions in the bulk.

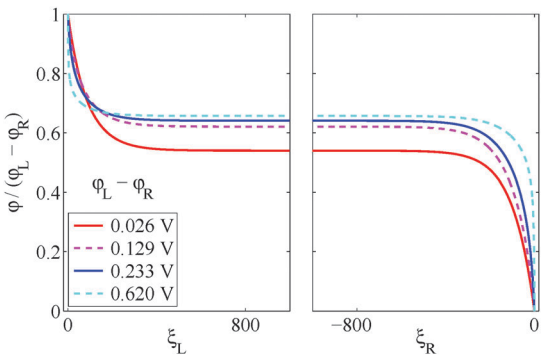

Fig. 4 Normalized electrostatic potential in the boundary regions L and R for different prescribed boundary values.

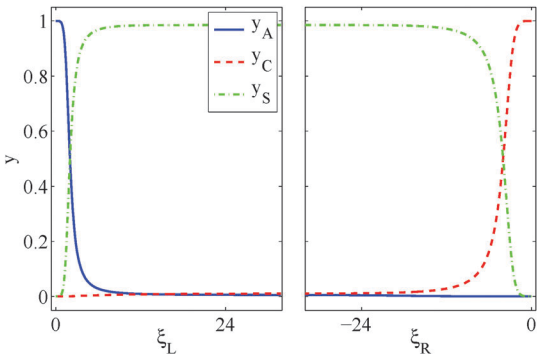

Fig. 7 Concentrations y_A, y_C and y_S in the boundary regions L and R for $\varphi_L - \varphi_R = 0.62$ V and $y_A = 0.005$, $y_C = 0.01$ in the bulk.

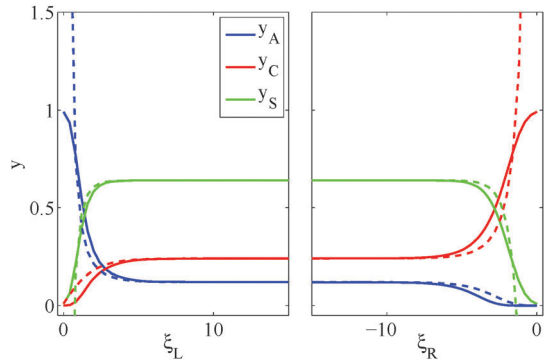

Fig. 8 Comparison of the proposed model (solid) with the Poisson–Boltzmann equation (dashed). The Nernst–Planck model does not guarantee $0 \le y_\alpha \le 1$.

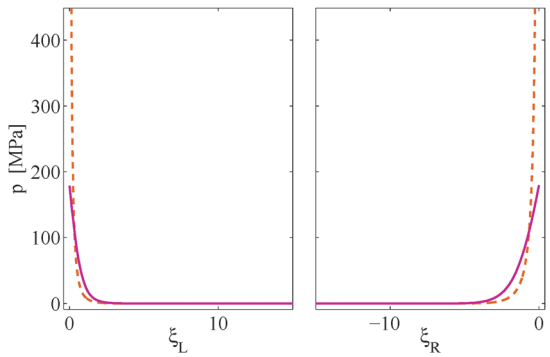

Fig. 9 Comparison of the proposed model (solid) with the Poisson–Boltzmann equation (dashed). The Nernst–Planck model and leads to far too high pressure in the boundary layer.

Finally we want to compare the proposed model with the classical Poisson–Boltzmann equation, where instead of eqn (129) and (130) we have in L and R

$$\partial_\xi \tilde{y}_\alpha + \tilde{y}_\alpha \partial_\xi \tilde{\varphi} z_\alpha = 0 \quad \text{for} \quad \alpha \in \{\text{A,C}\}. \tag{134}$$

In the algorithm above, we replace step 3 with the solution of

$$\partial_\xi \tilde{y}_\alpha^{j+1/2} + \tilde{y}_\alpha^{j+1/2} z_\alpha \partial_\xi \tilde{\varphi}^j = 0 \quad \text{in L and R, } \alpha \in \{\text{A,C}\},$$

with condition (133) for final or initial values respectively. We find that with the Poisson–Boltzmann equation alone, we are not able to guarantee that the atomic fractions y_α stay within the physical relevant domain [0,1], see Fig. 8. As a consequence the boundary layers are even narrower than in the model proposed here. Since in the Poisson–Boltzmann equation the elastic pressure is not controlled by the momentum balance, the computed pressure at the boundaries is too large by an order of magnitude, see Fig. 9.

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